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REQUEST
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54) Improvements to the compositions of vulcanisable rubber
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71) Requestor: Company named: BRIDGESTONE TIRE COMPANY LIMITED, resident of Japan
72) Invention of:
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This invention concerns a composition of vulcanisable rubber in which the efflorescence of sulfur is improved, and more particularly an improved composition of rubber obtained by holding sulfur in super saturation in the aforementioned composition at the state of dispersion.

In the preparation of rubber products, such as tires, belts, etc...it is often necessary to make the rubber adhere to rubber, or to different materials such as metal or organic fibers, and it is well known that the adhesion of non-vulcanized rubber affects the transformation and the productivity.

One of the causes of the reduction of adhesion of non-vulcanized rubber comes from the appearance of foreign materials, of an adhesion property much weaker than that of non-vulcanized rubber, in the portions and in the totality of the zone of adhesion of non-vulcanized rubber, due to a prolonged conservation, etc....which thus reduces a zone of anchoring between each material in contact and translates itself in the appearance of the phenomenon called efflorescence. In particular, the phenomenon of the efflorescence of the sulfur, used as an agent of vulcanization, considerably reduces the adhesiveness and the sticking power of the non-vulcanized rubber, and it is then highly desirable and indispensable to improve the efflorescence of sulfur in compositions of rubber.

The examination of the state of sulfur in the rubber during the course of the process of its preparation, with the aid of an x-ray micro-analyzer, an optical microscope, an electron microscope, and a scanning electron microscope, permits the establishment of a link between the mechanism of the appearance of efflorescence of the sulfur and the individual processes following the preparation.

With a view towards regulating the efflorescence of sulfur on the basis of the observations indicated below, it can be noted that according to the known processes, you can use, for example, insoluble sulfur as described in Japanese Patent No 13075/61, or a sulfur donor as described in Japanese Patents no 6096/72 and 6498/72 in order to prevent the dissolution of sulfur combined under the form of cyclic octagonal structure (S8) , in the rubber, as much as possible.....

(Process of molding and transformation)		(Mechanism for the appearance of the efflorescence of sulfur)
Cylinder of the Bambury Mixer-Extrusion on the calander	<Elevation of Temperature>	(A) The mixed sulfur (S) is dissolved in the rubber under the cyclic octagonal form (S8)
↓		↓
Cooling of the water – Rolling	<Super-cooling>	(B) S8 is in the state of super saturation in the rubber
↓		↙ ↘

Shrinking – Cutting		(C) Agglomeration of super saturated S8 at the surface of the rubber (formation of pockets on the surface)	(E) Collision by Brownian movement or internal agglomeration of the supersaturated S8 (formation of internal pockets)
↓		↙	↘
Rest until molding	<Rest>	(D) S8 in the rubber diffuses towards the pockets	(F) Growth of crystals in the interior of the rubber

...when the temperature is raised, or in order to prevent the S8 dissolved in the rubber to bring about a super saturated state and to precipitate by super cooling, while referring to the mechanisms (A) and (B) of the appearance of sulfur. However, given that the temperature of transition of insoluble sulfur to the S8 state is around 105° to 110 °C it is necessary to reduce the speed of calandering...

...or extrusion, so that the temperature does not exceed this transition temperature, particularly ion the calendaring or extrusion of the rubber at the highest module of elasticity. This results in not only a lowering of the productivity but also a disadvantageous deterioration in the power of dispersion of the insoluble sulfur itself. On the other hand, the use of a sulfur donor poses a problem of cost, and it has been very difficult up tot the present to practically and effectively regulate the efflorescence of sulfur.

While mechanisms (C) and (D) of the appearance of efflorescence of sulfur are brought about by the quantity and conditions of excitation and of resting temperature, during the course of the process, the formation of pockets of sulfur and the growth of crystals on the surface of the rubber, representative of the phenomenon of efflorescence, going back to the process of diffusion in which super saturated sulfur propagates on the surface of the rubber or throughout the interior of the rubber and begins to group together and to grow around the pockets. Given these findings, this invention is based on the reaction of S8 in the rubber with a tensio-active agent, in order to disperse and stabilize the S8.

The goal of this invention is a composition of vulcanisable rubber in which the efflorescence of sulfur is improved, obtained by adding a tensio-active agent to the composition of rubber to which sulfur has been added as an agent of vulcanization in a proportion of 0.5 to 10 parts per weight for 100 parts per weight of rubber, which can be either natural rubber or synthetic or a combination, in order to maintain the sulfur in super saturization during the state of dispersion in the interior of the composition of vulcanisable rubber.

The tensio-active agent suitable to this invention shows strong lipophilic properties, compatible with rubber, corresponding to an HL value (equilibrium hydrophilic-lipophilic) of 1 to 8, preferably 2 to 8, which represents the connection between hydrophilic and lipophilic groups. Examples of such tensio-active agents are given as esters of oleic, stearic, palmic, lauric acid with sorbitan, the esters of oleic and stearic acids with polyoxyethylene, polyoxyethylene-nonylphenol, stearate and laurate of diethylense glycol, etc.

If the HL value is less than 1, the affinity of the tensio-active agent towards the rubber is so greatly elevated that it is hardly absorbed in the interface between the rubber and the sulfur and it is dissolved in the rubber. While if this value is greater than 8, the affinity towards the rubber is so greatly weakened so that the quantity of the agent absorbed is weak, because of a partial absorption at the interface between the rubber and the sulfur, of a kind that a stable state can not be obtained without a long duration.

According to this invention, the tensio-active agent is added in the proportion of 0.1 to 150% in weight, preferably 0.5 to 100% in weight, with regards to the sulfur added as an agent of vulcanization. If less than 0.1 % in weight is added, this quantity is not sufficient to obtain a monomolecular absorption in the interface between all the sulfur and the rubber. While if more than 150% in weight is added, the physical properties of the rubber are altered.

According to the invention, the energy put into action is raised because of the crystallization of sulfur, and the stabilization by dispersion of the sulfur is difficult during a long duration. The invention then agrees with the cases where the duration of excitation at the surface of the rubber is limited by the action of cooling and at the beginning of the process of resting, as that of the extrusion in the process of preparation of the rubber.

Other ingredients besides sulfur can be added to the compositions of rubber in this invention, such as other usual agents of vulcanization, accelerators of vulcanization, promoters of vulcanization, agents of softening, antioxidants, strengthening charges, etc.

According to this invention, various types of synthetic rubbers can be used, such as rubbers made of polysoprene, polybutadiene, co-polymer styrene-butadiene, co-polymer acrylo-nitrile-butadiene, co-polymer ethylene-propylene, butyle and other similar rubbers.

The tensio-active agent added to the compositions of rubber according to this invention, does not produce any real effect on the physical properties of vulcanized and non-vulcanized rubbers.

The invention will be better including the reading of the detailed description which follows of several examples not limited to the various methods...

...of realization of the invention.

Examples 1 to 11

The various compositions of rubber indicated in table 1 are mixed, extruded across a cold die of the size 15.24 cm for tubes, cooled by water, excited by a process of shrinking, then left to rest for a duration of 1 to 3 days. The efflorescence was determined by photography through use of an optical microscope, and the zone of efflorescence was measured with an image analyzer (sold under the commercial name of "Orunicon" by the company called Shimazu Seisakusho ltd), to measure the rate of efflorescence for the surface of the rubber.

The various physical properties of the composition of rubber, vulcanized and non-vulcanized, were determined following the norms JIS K6300 and JIS K6301 and the results obtained are given in table 1.

These results show that the compositions of rubber in this invention, containing a tensio-active agent, present a large improvement in the efflorescence of sulfur, and, in addition, the physical properties of rubbers (vulcanized and non-vulcanized)are not appreciably modified, by comparison to those compositions not containing a tensio-active agent.

That being said, the invention is not at all limited to the examples described; it is adaptable to numerous variants accessible to experts, without moving away from the spirit of the invention.

Table 1 (1/4)						
Composition\mixture #	1 (comparative example)	2 (example)	3 (example)	4 (Example)	5 (exampled)	6 (Comparative Example)
Natural rubber	100	100	100	100	100	100
Carbon black HAF	50	50	50	50	50	50
Stearic Acid	2	2	2	2	2	2
Zinc Oxide	5	5	5	5	5	5
Antioxidant P (x1)	1	1	1	1	1	1
Accelerator of vulcanization NOBS (x2)	1	1	1	1	1	1
Sulfur	4	4	4	4	4	4
Insoluble Sulfur						
Tri-ester of Oleic acid and sorbitan		1.5				
Mono-ester of stearic acid and sorbitan			1.5			
Mono-ester of palmic acid and sorbitan				1.5		
Stearate of polyethylene					1.5	
Polyoxyethylene nonylphenol						1.5
HL value of various tensio-active agents	X	1.8	4.7	6.7	8.0	9.5

Table 1 (2/4)					
Composition\mixture #	7 (comparative example)	8 (example)	9 (example)	10 (Example)	11 (exampled)
Natural rubber	100	100	100	100	100
Carbon black HAF	50	50	50	50	50
Stearic Acid	2	2	2	2	2
Zinc Oxide	5	5	5	5	5
Antioxidant P (x1)	1	1	1	1	1
Accelerator of vulcanization NOBS (x2)	1	1	1	1	1
Sulfur					
Insoluble Sulfur	7	7	7	7	7
Tri-ester of Oleic acid and sorbitan		1.5			
Mono-ester of stearic acid and sorbitan			1.5		
Mono-ester of palmic acid and sorbitan				1.5	
Stearate of polyethylene					1.5
Polyoxyethylene nonylphenol					
HL value of various tensio-active agents	X	1.8	4.7	6.7	8.0

Table 1 (3/4)

Composition\mixture #	1 (comparative example)	2 (example)	3 (example)	4 (Example)	5 (example)	6 (Comparative example)
Results						
Efflorescence Rate (%) after 1 days rest	8.0	3.9	2.7	3.0	3.5	5.6
After 3 days rest	13.5	11.6	4.6	5.1	5.9	12.0
Mooney Viscosity (ML 1x4)	83		82	82	82	
Time of Mooney Rolling (mn)	18		17	18	18	
Hardness (degrees)	63		62	62	62	
Strength (%)	52		51	53	52	
Extension (%)	450		460	450	470	
100% Module (kg/cm2)	30		29	30	30	
200% Module (kg/cm2)	134		130	132	132	
Resistance to tension (kg/cm2)	240		250	240	240	

X1 N, N1-diphenyl-p-phenylenediamine
X2 N-oxydiethylene-2-benzothiazylsulfenamide
X3 Sold by Stauffer Chemical (CRYSTEX)

Table 1 (4/4)					
Composition\mixture #	7 (comparative example)	8 (example)	9 (example)	10 (Example)	11 (example)
Results					
Efflorescence Rate (%) after 1 days rest	10.0	7.0	7.3	8.0	8.2
After 3 days rest	15.0	13.0	12.0	13.0	13.2
Mooney Viscosity (ML 1x4)	75	74	75	75	75
Time of Mooney Rolling (mn)	10	9	9	8	10
Hardness (degrees)	74	74	73	73	73
Strength (%)	48	49	48	49	49
Extension (%)	270	265	270	275	272
100% Module (kg/cm2)	53	52	54	52	53
200% Module (kg/cm2)	132	130	132	135	130
Resistance to tension (kg/cm2)	200	205	202	210	215

Claims

1. Composition of vulcanisable rubber in which the efflorescence of sulfur is improved, characterized in that a tensio-active agent is added to a composition of rubber to which sulfur has been added as an agent of vulcanization in the proportion of 0.5 to 10 parts weight for 100 parts weight of rubber, which can be natural or synthetic or a mixture, in order to maintain the sulfur in super saturation at the state if dispersion in the aforementioned composition of vulcanisable rubber.

2. Composition according to claim 1 characterized in that the tensio-active agent has an HL value from 1 to 8, which represents a relationship of the equilibrium of the hydrophilic and lipophilic groups.

3. Composition according to claim 2 characterized in that the tensio-active agent is an ester of oleic, stearic, palmic, or lauric acid with sorbitan, or an ester of oleic or stearic acid with polyoxyethylene, or polyoxyethylene nonylphenol, or stearate or laurate of diethylene glycol.

4. Composition according to claim 1, characterized in that 0.5 to 150% in weight of the tensio-active agent can be added, in relation to the sulfur which has been added as an agent of vulcanization.